Toxicity issues pertaining to burning pyrotechnics

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Abstract

We all know that normal operations with pyrotechnic compositions or other energetic materials, apart from the desired effect (e.g.: controlled blast from high explosives, propulsive power resulting from propellant gas pressure, various visible or sound effects from fireworks…) lead to the release of various products (gases, vapours, aerosols) in the environment, in relation with the chemicals, the reactions involved and some physical parameters.

Although discussed from time to time by experts, and contrary to the case of 'conventional' fires [1], toxicity and environmentally related questions associated with burning pyrotechnics, have received far less attention than they actually deserve. Therefore, this paper supports an analysis of our current understanding of the sole toxicity problems (acute toxicity, sub-acute toxicity concerns…) emerging with all types of burning pyrotechnics, at the light of what has been established to address 'normal' fires in built environments. The paper provides an analysis of the regulatory context, lessons from past accidents, typology of chemistry and reactions of pyrotechnics, and some contribution to the analysis is supported by experiments on smoke powders, one significant family of products belonging to pyrotechnics. Eventually, a discussion is proposed to envisage pathways to go further in learning on those important issues.

1. Introduction

Pyrotechnic compositions present challenging issues in many aspects. Combustion related issues and safety considerations are no exception, and even in some well known cases look like controversial issues. For instance, the availability of first generation air-bags systems was considered as a major step in the reduction of car crash impacts on passengers. However in the same time, both intrinsic and non intrinsic combustion related toxicity issues have been raised, due to the type of gas generating energetic materials primarily used for their development, namely sodium azide [2][3]. Considering pyrotechnics in a more global scope, the extreme diversity of their applications (pyrotechnic compositions used in display and consumer fireworks, propellants and powders, 'special effects' systems (like distress flares, gas generators, smokes of all sorts), pyrotechnic devices for the automotive industry…) is by itself very challenging for coping comprehensively with all safety-related issues.

The analysis of toxicity issues proposed in this paper was motivated from the lead author's primary scientific background; that is 'conventional fire' safety. The so called 'conventional fires', are all those fire involving materials that burn by reaction with air in the so-called diffusive (laminar or turbulent) mode. They represent a large fraction (say 99%) of all fires taking place in any type of built environment. Fire safety science, and related fire engineering practice, were developed as early as in the late 1890's, when for instance, the NFPA (National Fire Protection Association), a non-for-profit organization solely devoted to reducing all types of fire threat (primarily of thermal nature) started to develop standards and codes. As compared to current knowledge in the field of pyrotechnics (those materials sometimes referred to as 'low explosives'), toxicity fire science constitutes by now a well advanced knowledge, and as a result, more interactive processes between scientific communities covering fire science, and those covering safety related issues of explosives, and pyrotechnics of all sorts is thought highly desirable [4]. This view is expressed despite significant differences in the reaction processes that are involved with burning pyrotechnics comparatively to conventional fire. This paper is an effort to contribute to such a process.

With the guidance brought to us by fire scientists on combustion-related toxicity issues, our purpose is therefore:

- to review what is the current knowledge on the matter regarding pyrotechnic compositions of all sorts, when reactions taking place and liberating chemical species do not lead to mass explosion.
- to review how those issues are currently handled by regulations or other means in some applications and provide some analysis on how to progress
- to explore capabilities of some experimental equipments (e.g. the US Fire Propagation Apparatus (FPA) so called 'Tewarson' Apparatus in France [5], other more conventional laboratory calorimetry techniques) to provide information on toxicity pertaining to burning pyrotechnics
- to discuss on how we should try to progress in the field in future research efforts.

2. Combustion-related toxicity of energetic materials and regulations

Control of the toxicity threat from regulation is currently very limited, if actually existing at all for pyrotechnics: Four main reasons for this situation can be quoted:

a) Combustion toxicity is by no means an intrinsic property of any material, as recalled long ago by Babrauskas [6]. Covering toxicity issues in case of normal or accidental burning of any combustible product through regulatory thresholds values referring to toxicity criteria is thus very often irrelevant, if appropriate 'combustion scenarios' cannot be well defined or characterized and if no satisfactory 'toxicity index' cannot be adequately developed.

b) Acute, or severe sub-acute combustion toxicity issues with pyrotechnics are probably limited to military applications [7] (normal use scenarios), or other very limited professional applications, and thus not relevant for a regulatory control by nature.

c) No significant threat - contrary to what was deducted from the post mortem blood analysis of victims of fires involving ordinary materials in buildings- could so far be assumed from experience with most pyrotechnic compositions

d) Until recent past, validated knowledge seems to be limited to energetic materials in use for blasting operations in underground mining, where most often toxicity problem are related to fast thermal decomposition reactions of nitro-compounds, thus liberating essentially toxic species such CO and NO_x. For instance, example of studies regarding the parameters affecting the yields of NO_x and CO emitted have been carried out by Mainiero [8][59].

As an example, in the context of the Canadian regulatory scene, carbon monoxide plus nitrogen oxides emitted by basting agents or high explosives are referred to as fumes by the explosive industry. A classification containing three classes of those materials have been established according to specific test conditions [9] on the quantity of fumes produced. Only class 1 explosives (limiting the emissions of fumes to less than 22.6 L/kg of cartridge of given geometry) should normally be used in underground applications. On the European side, long term collaborative research ended up with the implementation of national limits for a toxicity index taking account of CO and NOx emissions based on the application of the standard EN13631-16 [10]for same usage (underground mining).

By comparison, a similar situation appears regarding the control of toxicity issues in accidental 'normal' fires. Regulators have often felt reluctant in the past to set regulations for the control of the non thermal fire hazard, with a few exceptions, like in the transportation sector (aeronautics, railways), where prompt evacuation of occupants of concerned enclosures (rail cars, aircraft cabin) are not a potential emergency response, in case of a fire. As an example of this, the French subways and railways operators require that materials used in rail cars fulfil requirements defined in combined French standards [11], [12].

As a result of numerous studies of the kind carried out on both side of the Atlantic Ocean, regulators have developed requirements

expressed in terms of maximum threshold values for the sum of [CO + NO_x] for mining applications.

To our knowledge [13], limitation of toxic yields from burning pyrotechnics exist only for air-bag inflators. In that case, the toxicity problem was an issue identified in the early stage of development of such safety car components, due to both inherent toxicity of sodium azide, the first gas generating material that was used, and from combustion / decomposition related toxicity.

Further reduction in combustion toxicity obtained from use of new blends of chemicals such as compositions with complexes of transition metals [3][14], together with other performance targets such as increase in gas production rates, is still in the current research agenda of developers [15]. However, target limits are driven by the automotive industry proprietary standards, and thus, due to competition, test data on toxic emissions from the various pyrotechnic compositions in use are not easily made available in the public domain.

We might have to face in the near future an increasing societal demand, in particular impacting the firework industry, for knowing more about actual concerns that might arise from repeated exposures of diluted smoke in the environment of the workers (professional of display fireworks) and of the public. This could, in turn, initiate some move from the regulatory scene in this sector.

3. Fire Toxicity: brief overview of state-of-the-art

About three decades of research have been dedicated to the study of toxicity of fire effluents. In this time, it has been recognized that the bulk of fire victims generally die from toxic smoke inhalation rather than from thermal burns (Alarie [16]). Prominent researchers in the field during that period of time have been Hartzell [17], Purser [18], Alarie, Tsuchyia [19], Levin [20], Baud [21], Gann [22], and some others. Recent overviews are available that correctly summarize current knowledge as well as workable tools for use in toxicity risk assessment (see also the recent international standards being produced by ISO TC 92 SC3, progressively replacing the old reports series produced in the late 80's [23]).

From their work and findings, the following is of interest, in terms of knowledge transfer to the scientific community of pyrotechnics:

- Acute toxicity in fire always results from multiple components exposure that superimpose to other environmental parameters (temperature, stress, health conditions of exposed people…),
- Figure 1 expresses the Haber's rule often considered for individual toxic fire component stating that a given effect (e.g. lethality) is a function of the dose (time x exposure) received.

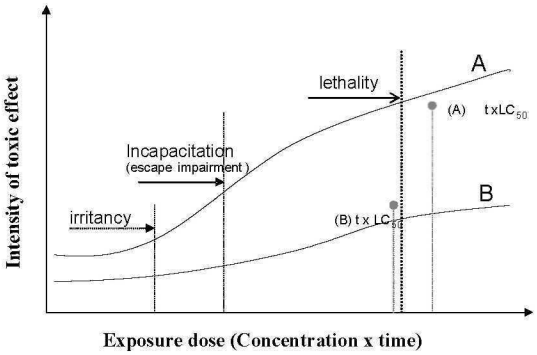


Figure 1: Dose-response relationship of fires for 2 substances 'A' & 'B': the basic paradigm of fire toxicology (adapted from Pauluhn [24])

- Although hundreds of components are emitted in fires, a limited number of them are responsible for actual acute toxicity threat, that can be classified into :
  a) asphyxiant, or narcosis-producing toxicants (CO, HCN, CO_2, limited O_2)
  b) sensory or pulmonary irritants (NO_X, SO_2, HCl, HBr, aldehydes, particles…)
  c) toxicant exhibiting other or unusual effect (e.g. neurotoxics, carcinogen effect…)
- In most cases, CO levels were found high enough (in terms of carboxyhemoglobin – COHb- in blood samples from the bodies) to be assumed as the primary cause (if not the unique cause) in fire deaths occurring in built enclosures; rare other situations have been identified where HCN or SO_2 [1] played the main role in 'conventional fires' casualties.

- To a reasonable approximation in most cases, the effects of major toxic components may be considered as additive for situation of interest with asphyxiants and irritants, although the real effects comprise more complex synergisms and even in some cases antagonistic effects [20/21].
- These latter results have led to the development of the fractional effective dose (FED) model, that expresses this concept in its simple form according to equation (1):

$$FED = \sum_{i=1}^{n} \int_{t_1}^{t_2} \frac{C_i}{(Ct)_i} \Delta t \qquad \text{(Eq. 1)}$$

Where in the summation, any C_i term stands for the concentration of toxic species i taken into consideration, and $(Ct)_i$ stands for the critical dose related to that species i for a given effect (e.g. lethality). When the FED value reaches 1 in a given scenario, the toxic effect intensity is assumed to be obtained. Considerations on the validity of this type of equation for various types of exposed sub-populations have been reported by Hartzell [25]. Equation (2) is the simplest form taken by the FED model when assuming the toxic threat is limited to CO + HCN.

$$FED = \int_{t_1}^{t_2} \frac{[CO]}{35000 ppm \cdot min} \Delta t + \int_{t_1}^{t_2} \frac{\exp([HCN]/43)}{220 min} \Delta t \qquad \text{(Eq. 2)}$$

Equation (2) also reflects the fact that the dose-effect relationship followed by the HCN species do not actually follow the Harber's rule, concentration level 'weighing more importantly' than exposure time in that case.

In contrast, equation (3) is the more complex but still workable equation that may be used by fire engineers to analyse the risk of incapacitation in built environment that can arise from the combination the following irritant species:

$$FEC = \frac{[HCl]}{F_{HCl}} + \frac{[HBr]}{F_{HBr}} + \frac{[HF]}{F_{HF}} + \frac{[SO_2]}{F_{SO_2}} + \frac{[NO_2]}{F_{NO_2}} + \frac{[acrolein]}{F_{acrolein}} + \frac{[formaldehyde]}{F_{formaldehyde}} + \sum \frac{[Irritant]_i}{F_{C_i}} \qquad \text{(Eq. 3)}$$

- The concept of lethal potency (that is the toxicity of the smoke (gases +aerosols) from a specimen of material or product, taken on a per unit-specimen-mass basis, depicted by the symbol 'LC_{50}') has been developed to account for the concentration which will be lethal to 50% of the exposed subjects. LC_{50}'s are accessible from experiments including bioassays using animals as well as through estimates derived from lab-scale combustion experiments on materials, and from use of models (eg. ISO 13344 [26]), based on existing animal test data, according to measured concentration of toxic species in the smoke environment.

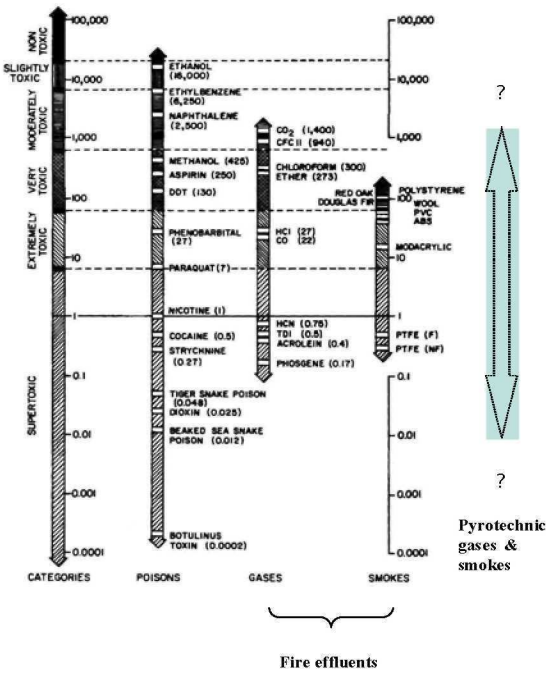


Figure 2: Range of toxicity potencies for combustion products as compared to other poisons –(adapted from Hirschler, 1987 [27])

Figure 2 gives an overview, in arbitrary units, of the toxicity issues pertaining to conventional products emitted in conventional fires (gases and smoke), confirming their toxic potency and providing some ranking between toxic species. Figure 2 also illustrates that "actually supertoxic" fire effluents, that were in

focus in the past in fire research are extremely rare. This is indeed one of the interests of the LC_{50} concept (when coupled with bioassays), that allows rapid identification of combustion-related extra-ordinary toxicity issues, during early stages of new materials or products development [22]. Very few problems of this kind were reported in the literature in the past, like the cases known exceptions regarding PTFE smoke particles and an organophosphorous caged compound identified in a burning test involving a fire-retarded polyurethane foam [28].

However, unpublished cases may have also occurred during R&D work performed by the chemical industry ([29])

Indeed, we have currently no precise idea on how 'pyrotechnic smoke' (limited to the aerosol components) is ranking relatively to the other products listed in Fig. 2. Last but not least, it has been established (e.g. by Babrauskas [30]) that Lethal potencies of 'conventional fire' smoke doesn't vary much, contrary to rate of smoke production depending on materials and scenarios, which in turn makes the real difference. That is why fire scientists are focusing on obtaining basic fire data such as mass burning rate per unit area and yields of combustion products emitted (in mg/g) to characterise 'source terms' of non thermal damage potential, in addition to estimate of some kind of critical toxicity value for species of interest. Many searchers have produced such data for various materials. A compilation of such data for burning chemicals was recently published by Tewarson & Marlair [31].

4. Analytic analysis from chemistry of pyrotechnics

Pyrotechnics highly differ from classical combustible materials in many ways, and thus a careful examination and comprehension of their chemistry and reaction modes under normal use or accidental scenarios are needed to identify and evaluate toxicity issues relating to species emitted in pyrotechnics gases and smoke.

One of the basic differences is that most of the time, if not in all cases, pyrotechnic compositions intimately mix combustible materials (carbonaceous, sulphur, phosphorous, metals, others…) with oxidisers (nitrates, perchlorates, chlorates…). Thus, the community of pyrotechnics knows very well, from information available in the references [32] to [33], the high variety of possible pyrotechnic compositions according to applications (industry of fireworks, distress signals, propellants for military or civil use, special effects).

Table 1 (from [4]): color-governing chemicals in pyrotechnic compositions

Chemicals or chemical element	*Flame color obtained*	*Light intensity*
Li	carmin red	intense
Na	yellow	intense
K	purple pink	weak/average
Sr	red	weak/glow
Ba	green	weak/glow
CaCl	orange red	intense
SrOH & SrCl	red	intense
BaOH &BaCl	green	intense
CuOH	green	intense
CuCl	blue	intense
BO_2	green	intense
Mg, Al	bright white	intense

Some 300 different pyrotechnic compositions have also been compiled and made available on the web according to the initiative coming from the Netherlands [34].

As a reminder, when coloration of the effect is the issue, the chemistry of the composition will vary according to desired color and luminous intensity. Potential chemicals that may be used (as an example!) are indicated in table 1.

Table 2 was prepared from ref. [35] to [37]. It lists and classifies products emitted that may contribute (with highly varying weights) to the overall potential toxicity arising from those products when burning, according to typical pertinent scenarios.

Table 2 : Significant products emitted from by reaction of pyrotechnics (fireworks only)

type	chemicals emitted
gases	CO_x, H_2, H_2S, CH_4, COS, CH_4, N_2, NO_x, O_2, SO_2, …
aerosols	Al_2O_3, $(NH4)_2CO_3$, Sb2O3; BaCO3, BaSO4; Bi2O3, C (charcoal), CuO, Fe2O3, MgO, KCl, K2O, K2CO3, KNO3, K2SO4, K2S, K2SO3, KCNS, SrCO3, SrSO4, S, TiO, …

4.1 What do we know so far from accidents and testing ?

Regarding the fireworks industry, statistics recorded by the NFPA [38], as well as other information sources from recent well known accidents (Enschede, NL, 2000 [39], Kolding DK, 2004 [40] [41]essentially stress that most (if not all) victims are the results of burns and blast effects in case of accidental mass detonation, or possibly, in some cases, from the consequences of physical impacts of projectiles. However, in both mentioned worst-cases, some medical treatment has been required for a few inhabitants leaving close to the premises or fire-fighters just after the accident. To our knowledge, relating symptoms did not apparently end up for those patients with persistent troubles.

In addition, more scientific feedback was made available as the aftermath of a measuring campaign implemented during and just after the accident of Enschede [42]. The study consisted in taking samples on the day of the fire and on the following days to perform analytical measurements of toxic/pollutant species. The results, which refer to three different phases for the data acquisition provides clear indication that a number of species were present in concentrations that significantly exceeded so-called 'long term acceptable limits' quoted for a comparison in the report. According to that report, the bulk of the substances and chemical elements at the origin of the gaseous and solid emissions are as follow (table 3)

Table 3: main materials (termed in related elemental quantities) involved in the Enschede fireworks accident [42]

materials/elements	quantities (kg)
Carbon based (as C)	1150000
Pb	22000
Cu	13000
Zn	21000
Ba	2200

Table 4 summarizes part of the analytical results from the study that focus on those species that, at some time during the accidental scenario, were measured in quantities exceeding what is referred to as admissible long term threshold values in the report.

Table 4 : concentrations of toxic species emitted during the Enschede accident (after table 5.1 in ref. [42])

Toxic species	Concentrations vs phase (1, 2 or 3) of accident (µg/m3)			long term value
	1	*2*	*3*	
PM_{10}	135	1045	290	40
Cu	3.6	2.6	-	0.9
(Mn)			(2.2)	0.6
Ba	6.5	-	2.1	1
Pb	1.5	23.1	2.8	0.5
Cd	-	0.7	-	0.3
Cr		0.07		0.0025 (a)

(a) : admissible long term value refers to Cr^{6+}

Other type of pyrotechnic materials would deserve further consideration as regards the combustion related toxicity issue. For instance, normal use and accidental burning of propellants based on AP/HTPB systems essentially raises the question of HCl emissions. Although some work has been done in the field [36] [37] [56]…, we are still lacking consolidated data on burning behavior of black powder, an essential constituent of lifting and bursting charges in fireworks devices. Within the automotive industry, the initial toxicity issues relating to sodium azide and related decomposition products have somewhat shifted to the control of other types of toxic species according to propellants under development and from controlling oxygen displacement by N_2 generation

Finally, another type of pyrotechnic compositions, those in use for generating "more or less buoyant "smokes" (e.g. screening effects for military applications), may cause well identified potential concerns regarding toxicity . At first, smoke compositions have been reported to often contain inherently toxic products [33]. In addition, acute combustion-related toxicity have been recently proven by a detailed study on given smoke compositions [43]. In the latter case, products of concern were essentially organic compounds that also raise the carcinogenic risk issue. Survival fractions of such organic compounds, that much often present irritant properties, are generally very

limited in temperature environments exceeding 500 to 700°C [44].

5. Experiments on smoke powders

5.1 Test materials

Two different smoke powders consisting in ternary mixtures containing starch and lactose as fuel components and potassium nitrate as an oxidizer have been supplied to investigate the potential toxicity concerns arising for their use as "clean smoke" generators.

Such compositions are currently in use by the Fire Services in Switzerland and France for the control of smoke venting systems in buildings. The characteristics of the two test smoke powder samples used in the test series are indicated in table 5.

Table 5: composition (mass %) of test smoke powders

components	SP1	SP2
lactose	30%	22.5%
starch	30%	22.5%
KNO_3	40%	45%

(Notice : 'SP' stands for smoke powder)

5.2 Experiments conducted by INERIS using of the Fire Propagation Apparatus

5.2.1 The FPA or Tewarson Apparatus

A Tewarson calorimeter (see fig. 3) was commissioned in a dedicated laboratory by INERIS in 1997. Designed in its early configuration as soon as the mid 1970s (Tewarson and Pion, [45]), the current version has significant advantages, having benefited from more than 20 years of development and technical improvements. Associated test protocols give access to information on fire related phenomena of a qualitative nature (visualisation of product specific phenomena, or characteristic flame colour changes etc.) as well as of a quantitative nature (rate of heat release, mass loss, smoke opacity, etc.) that can be obtained for a large variety of materials.

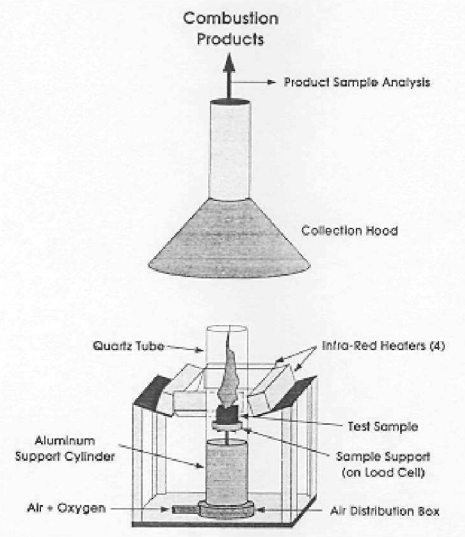


Figure 3 : schematic view illustrating the operating principle of the Fire Propagation Apparatus (FPA)

The equipment has received more official recognition by standardization bodies like ASTM and NFPA [5], and has quite recently been added in the limited list of equipment that have been recognized capabilities in the field of fire toxicity issues by ISO TC92 SC3 (Technical Committee regarding Fire threat to people and the environment [46]).

Research work devoted to the exploration of the potential use of the equipment for other goals than learning on the fire behavior of polymeric materials [47] has been the main target with the use of the apparatus in Europe [48].

Preceding experience with the equipment at INERIS regarding evaluation of the hazards presented by energetic materials comprises: a) the fire behavior of organo-phosphourous pesticides [49], b) the evaluation of toxic emissions of electrolytes for large electric capacitators, c) the analysis of the decomposition processes of nitro-cellulose based archive films and d) the evaluation of toxicity issues presented by mixtures containing incense /oxidizers mixtures.

Moreover, fire-induced toxicity properties of chemical additives is also in INERIS research agenda with this apparatus [51].

At last, quite surprisingly, the inventor himself contributed to the evaluation of the potential use of the apparatus in the area of energetic

materials by characterizing the fire-enhancing properties of different oxidizers [50].

Figure 4: Smoke Powder 1 burning in the Tewarson apparatus operated by INERIS

5.2.2 Experimental results with Smoke Powders

Table 6 summarises the main results obtained from tests under controlled combustion conditions, representing well ventilated fire conditions, in the Tewarson apparatus. Samples weighed some 80 g and were distributed in circular glass pans (88 mm in diameter). Ignition was obtained from a pilot flame without use of the external heat flux system see figure 4).

From those results, it can be noticed that a significantly faster combustion process is observed from the mass loss rate measurement leading to a specific rate of combustion of some 400 $g/m^2/s$ with the powder SP2, containing 45% KNO_3 against only 140 $g/m^2/s$ in the case powder SP1 only containing 40% of KNO_3.

Regarding the emissions, as expected from the low temperature of the combustion process, which characterises most smoke producing pyrotechnic compositions presenting obscuring capabilities, a number of irritant species are produced in such quantities that the toxic hazard assessment requires more in-depth analysis – taking into account practical scenarios of use- to conclude on actual dangers relating to the proven toxic potency revealed from the tests.

Table 6 : combustion characteristics and products released from burning Smoke Powders in the Tewarson apparatus

Combustion products	SP1	SP2
	40% KNO_3	45% KNO_3
	Combustion rate ($g/m^2/s$)	
	140	400
	Emission yields (mg/g)	
CO_2	690.2	700.4
CO	98.2	56.4
Total hydrocarbons	16.2	6.8
NOx	5.5	4.2
Soot	19.5	18.2
Ammonia	10.8	4.6
Methylamine	< 0.04	ND
Dimethylamine	D	D
Trimethylamine	D	D
Formaldehyde	0.380	0.283
Acetaldehyde	1.299	0.318
Acrolein	ND	ND
Pentanal	D	0.003
Butanal	0.016	0.004

5.2 Experimental conditions for DSC experiments on Smoke Powders and corresponding results

A TA Instruments Q-1000 differential scanning calorimetry (DSC) was used to study the thermal behaviour of the same smoke powders in air and nitrogen. About 1-2 mg of smoke powders were placed in aluminium pans sealed with pin-hole lids.

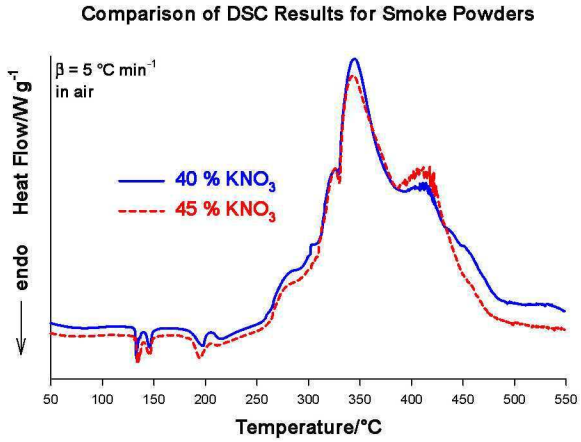


Figure 5 : DSC results on Smoke Powders

The samples were heated from 40 to 550 °C at 5 °C min^{-1}. Experiments were carried out in a dry air or nitrogen purge at 50 cm^3 min^{-1}.

The DSC was calibrated for heat flow [54] and temperature [55].

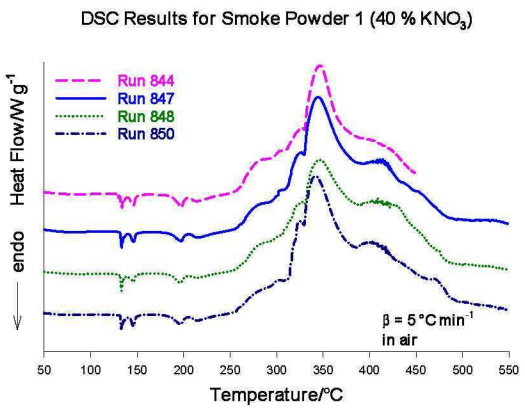


Figure 6 : DSC results on Smoke Powders, repeatability analysis

Figures 5 to 7 report on some graphical results obtained on smoke powders with DSC experiments.

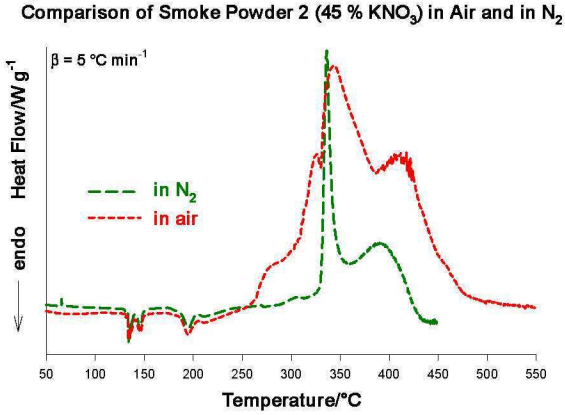


Figure 7 : DSC results for SP1 in air and N_2

5.3 Experimental conditions for TG-DTA-FTIR-MS experiments on Smoke Powder and relating results

A TA Instruments 2960 simultaneous TG-DTA was interfaced to a Bomem MB100 Fourier Transform Infrared (FTIR) Spectrometer and a Balzers Thermostar GSD300 Quadrupole Mass Spectrometer (MS). The TG-DTA-FTIR-MS data were acquired simultaneously to study the thermal behavior of the smoke powders and to identify the gases that evolved while the samples were heated.

Equal amounts (5 mg) of sample and reference material (Pt foil) were placed in alumina pans and heated at 10 °C min^{-1} to 1200 °C in air (50 cm^3 min^{-1}). TG mass, DTA baseline and temperature [55] calibrations were performed prior to the experiments.

The FTIR interface consisted of a 5 mm i.d. Teflon tube and a 10 cm Pyrex cell with a 50 mL volume and KBr windows. A quartz microfibre filter was placed at the FTIR inlet. The acquisition rate of the FTIR was one scan every minute.

For the MS analysis, the heated quartz capillary interface was placed near the sample pan, in the TG-DTA furnace. Data were acquired using bargraph scan, from 29 to 300 amu (atomic mass unit) at a speed of 0.2 s/amu. The electron multiplier detector was set at 960 V for acquisition. The MS was calibrated for mass alignment and amplifier signal.

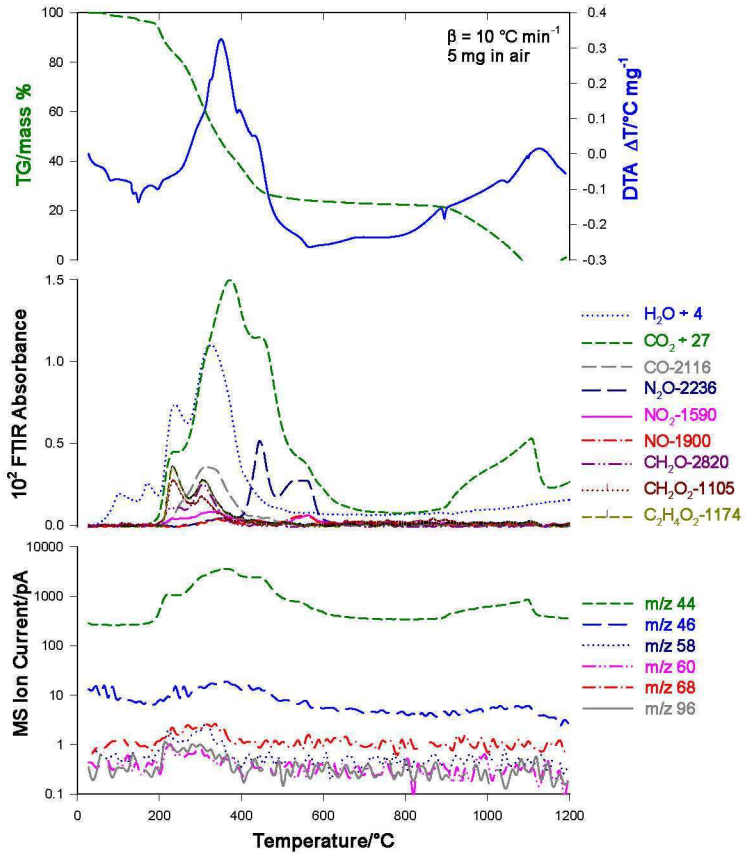
5.4 Brief analysis of test results.

The experiments relying on the use of the Fire propagation Apparatus (FPA) (see table 7.) confirm –if needed- the high degree of polyvalence of such an apparatus to address in a reasonable way thermal as well as non thermal issues regarding building and industrial fires, including atypical combustion processes, provided that the rate of reaction is not to high, and that no significant pressure build-up is taking place. From previous experience achieved by Tewarson himself and by INERIS, we may think that the decomposition is representative of most of effects induced in the 'real world' burning processes. On the materials tested, they reveal the potential for such substances to emit irritant substances such as aldehydes in quantities that have to be taken into consideration, even if they are normally absent in high temperature combustion processes, [44]. The second main information is that the concentration in the oxidizer agent (KNO_3) plays a role in modifying rate of reaction as well as yields of species emitted.

The other tests were also useful to identify or confirm that the experimental technique may highly influence the results (at least at lab-scale). The DSC tests (figure 5) did not show much difference in the decomposition behavior of the two smoke powders (contrary to FPA), which may find an explanation in the fact that the heating rate is not representative of 'burning pyrotechnics' like smoke powders. The lack of difference for the two smoke powders may also

be due to the much smaller sample size used in DSC measurements: the sample size used in the FPA is at least 4 x 104 times larger than that used in DSC. On the other hand, DSC results (see figure 7) show that air may play a role in the case of smoke powders, despite of the general assumption presented in table 7.

There are also no significant differences observed for the thermal decomposition of the smoke powders from the TG-DTA-FTIR-MS results. Similar to DSC, the low heating rate and small sample size used in TG-DTA-FTIR-MS are probably the causes of this lack of difference. Coupled TG-DTA-FTIR-MS results (figure 8) are more illustrative of the interest of coupling different experimental techniques to investigate such a complex issues as combustion related non thermal damage pertaining to reactive materials when burning. Qualitative identification of species emitted from TG-DTA-FTIR-MS tests reveals how powerful those techniques are to perform relevant screening tests with reasonable time/cost efforts. Next step will be to proceed to further investigation by coupling same analytical techniques to flash pyrolysis technique, which use a high heating rate closer to smoke powder burning process.



SP1.768: a) TG-DTA; b) FTIR; c) MS results for 5 mg INERIS Smoke Powder 1 heated in air at 10 °C min^{-1}.

Figure 8 : Evolution of TG-DTA/FTIR/MS results for smoke powder 1 (40% of KNO3) according to common temperature range

6. Discussion

We have shown from preceding development that burning pyrotechnic toxicity issues do exist, although we may reasonably think that acute toxicity concerns resulting from normal use of pyrotechnics are essentially existing in military applications (eg. smoke powders containing hexachlorohexane…). However, to get a better understanding on all 'non thermal' issues of burning pyrotechnics, from acute toxicity up to environmental

pollution and contamination related problems, more knowledge-based information must be produced in order to provide satisfactory data for analysing adequately those issues and be able to evaluate toxicity related problems for cases of interest.

In particular, likewise for the case of conventional fires [52][53], repeated exposure more to sub-lethal doses of pyrotechnics smoke might be of concern. The evaluation of such situations (that occur at least for workers, if not for the public with display fireworks shows, and possibly also with smoke producing pyrotechnic compositions and other applications making use of pyrotechnics) must rely on a more in-depth analysis, by producing suitable new information (from test data, new lessons from experience…).

Due to the high variety of pyrotechnic compositions, the importance of toxicity related issues is likely to vary somewhat according to products and applications, so a case by case approach is probably the best method for addressing properly the question. INERIS and CERL have just started to collaborate in such a direction, by examining (see section 5) experimentally the case of smoke powders.

In the near future, other tests with different compositions will be carried out, in the framework of a commonly supported thesis work, to which the University of Edinburgh (UK) (school of electronics and fire engineering) is also associated. The thesis work aims at developing analytical and experimental procedures to learn more on safety issues pertaining to non explosive burning of pyrotechnics. The importance of toxicity issues is also likely to be highly scenario-dependant:

- normal uses of pyrotechnics with single or repeated exposures to diluted pyrotechnic smoke may represent one generic type of scenarios
- accidental pyrotechnics smoke releases of all sorts are the second ‘generic’ type of scenarios to be treated

Subdivisions of both categories of mentioned scenarios will have to be correctly identified (for instance ‘high’ and ‘low’ temperature systems, ‘in-door’ and ‘out-door’ use of pyrotechnics, accidental burning inside enclosures or in the open…).

Table 7 might serve as a guideline to develop adequate research trying to optimize the findings obtained by fire researchers. This table simply outlines significant differences that can pertain between conventional fires and burning pyrotechnics scenarios.

Table 7 : conventional fires versus burning pyrotechnics: a comparison of governing paramaters affecting toxicity

parameters	conventional fires	burning pyrotechnics
chemistry of combustible materials	*Building fires :* CH-, CHO-, CHON- based natural or synthetic polymers (+ small amounts of Cl, S…) *Industrial fires* : largely more variable in terms of chemical structures and chemical elements involved	C (charcoal), C_xH_y, $C_xH_yO_z$, metallic powders, S, P, other organic materials (saw dust, wax…)
oxidizing stream	air	solid oxidizers intimately mixed in pyrotechnics compositions (nitrates, chlorates, perchlorates, mainly inorganic…)
mode of burning	diffusive burning in air	decomposition / 'combustion' in kind of deflagration mode (at least one order of magnitude higher in speed)
main toxic products identified (acute/sub-acute)	CO, HCN, depleted O_2 SO_2, HCl Other irritants (acroleine, aldehydes, isocyanates…)	metallic compounds (oxides or salts) with mercury, lead, arsenic…? irritants or products of specific toxicity (aldehydes…) with low temperature systems needs further evaluation to balance current positions
role of air	of prime significance: availability of air governs type of fire: - either fuel-rich (well ventilated) - or full lean (under-ventilated) [57]	limited role (in most cases) to: - burning of pyrotechnics packaging devices and materials - lifting charges ?
importance of aerosols/particles	limited for the acute toxicity problem. Under 10 µm, may however serve as carriers of adsorbed species inside the respiratory tract	significantly higher importance, as many of the products during burning of pyrotechnics are released as solids or solidify very quickly with decreasing temperature
Geometry of sources	Materials when burning can generally be assumed as fixed 'sources terms' of pollutant or toxic species	often to be taken as moving sources species, due to lift charges for many fireworks
pertinent lab-scale tools	So-called fire physical models with bioassay coupling capacities and lab-scale fire calorimeters (such as the FPA) Well identified in literature and standards (see in particular ISO DTR 16312-2 (2006) [46]	no pertinent standardized testing tool isolated initiatives existing, however.

The importance of toxicity issues is also likely to be highly scenario-dependant:

- normal uses of pyrotechnics with single or repeated exposures to diluted pyrotechnic smoke may represent one generic type of scenarios
- accidental pyrotechnics smoke releases of all sorts are the second 'generic' type of scenarios to be treated

Subdivisions of both categories of mentioned scenarios will have to be correctly identified (for instance 'high' and 'low' temperature systems, 'in-door' and 'out-door' use of pyrotechnics, accidental burning inside enclosures or in the open…).

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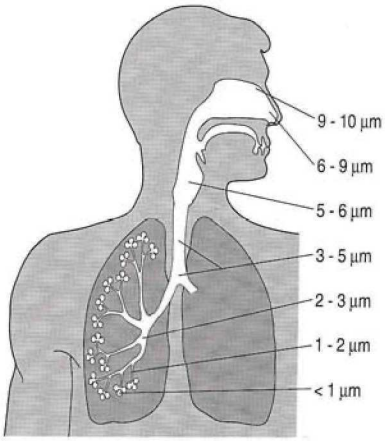

Figure 9 : inhalation pathways of aerosols according to particle size

As indicated in the mentioned table, aerosols must also be taken into account in the analysis.

However the complexity of the analysis of the toxicity issues pertaining to the aerosols emitted in burning processes is illustrated in figure 9, that first explain why 'PM_{10}' (particulate matter below 10 µm) may be of concern. The finer the particles are, the deeper they may penetrate into the respiratory tract up to direct interactions with cells in the lungs. Regarding that issue, new information is needed for both conventional fires and scenarios involving burning pyrotechnics, as indicated in recent analysis by Arntz [58].

Indeed, in the case of pyrotechnics, high temperature systems toxicity issues are probably more dependant on the size of the aerosols.

7. Conclusions

The current understanding of combustion-toxicity issues of burning pyrotechnics has been reviewed, with state-of-the art knowledge of related issues pertaining to 'conventional fires' serving as a guideline in the analysis.

From existing -and still very limited- information based on testing, past experience regarding normal and accidental scenarios where pyrotechnic materials are burning, acute toxicity issues seem to be limited to a number of more or less well identified cases (devices providing screening smoke for military application, possibly also 'first generations' air-bag inflators making use of sodium azide and other propellants).

However, existing knowledge regarding toxicity related issues of pyrotechnics are far less advanced than in the case of combustible materials burning with surrounding air in built enclosures or in the open. Moreover, studying combustion toxicity issues pertaining to pyrotechnics appears to be more complex due to the much higher diversity in chemistry and combustion processes exhibited by these materials, as compared to normal fires involving common materials.

Therefore, research efforts in the area are highly desirable and they may benefit from some of the engineering tools developed to study more general fire safety issues.

Our experimental contribution to support such an effort regarding the behaviour of smoke powders confirms that powders containing KNO_3 may present sub-acute toxicity issues, depending on scenarios of use.

Our understanding is that generally, those pyrotechnic devices leading to 'low temperature' decomposition or combustion processes, in order to produce special effects like screening are of concern, as they are liable to produce significant amount of organic irritants (like aldehydes) or organic species of specific toxicity (carcinogenic substances…). These tests have also proven the capacity and the interest of combining experimental techniques so-called 'fire calorimeters' (such as the Fire Propagation Apparatus) to more conventional calorimetry techniques coupled with MS/FTIR systems.

At last, we keep on thinking that closer collaboration between the scientific community of fire science and those relevant to energetic materials would be of mutual benefit (for instance for the development of validated sampling and analytical techniques for aerosols produced by combustion / decomposition processes).

8 Acknowledgements

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